Engineering and Process development

Extraction of Lactic Acid from Water Solution

BY AMINE-SOLVENT MIXTURES

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Although lactic acid can be made by fermentation from inexpensive raw materials, it is at present fairly costly, partly because of the costs of recovery and purification. The present study was undertaken to investigate a process which might reduce these costs.

The results suggest that it will be commercially possible to extract the lactic acid from the aqueous fermentation liquor by neutralizing the acid with an organic tertiary amine and then extracting the lactic acid–amine salt with an organic solvent. Triamyl- and trioctylamine were effective amines, and chloroform and alcohols were good extraction solvents. Tertiary amine–chloroform mixture extracted more than an equivalent amount of lactic acid. Alcohols are of interest because of the possibility of making the lactic acid ester directly from the salt.

An efficient and low-cost extraction process for the recovery of lactic acid from crude dilute aqueous solution would materially enhance the position of lactic acid as a large-volume chemical intermediate.

ALTHOUGH lactic acid is readily made by fermentation of inexpensive carbohydrates (*11*, *12*) and is relatively inexpensive in the crude grades, the price of the refined acid is high.

Thus, 44% technical grade acid costs 25 cents a pound (100% basis), whereas 85% National Formulary grade costs 81 to 85 cents a pound (100% basis) (*1*). This large spread in cost between the crude and refined grades suggests that any improvement in production or recovery methods leading to a reduction in costs would materially improve the position of pure lactic acid as an industrial raw material (*7*). The possibility of one such improvement, through esterification of the crude acid, has been pointed out by several workers (*5*, *6*, *14*, *19*). Still another possibility is the esterification-extraction process of Dietz, Degering, and Schopmeyer (*3*).

Extraction of lactic acid from water by solvents has also received attention from several investigators, who studied isopropyl ether (*9*), isoamyl alcohol (*10*), amyl alcohol (*18*), nitroparaffins (*17*), and several other solvents (*11*). Some refined lactic acid has been produced in this way (*12*), with isopropyl ether (*9*) as the solvent. Solvent extraction in general, however, is handicapped by unfavorable distribution coefficients (*11*) and, in the case of isopropyl ether, by the danger of fire or explosion (*16*).

It occurred to the authors that an improved recovery method might be based on extraction of the aqueous acid with a water-insoluble solvent containing an organic base. This view was supported by the work of Smith and Page (*15*), who extracted several acids, including lactic, from water solution with organic solutions of tertiary amines.

The authors have found that tertiary amines in water-insoluble organic solvents, including chloroform and alcohols, extract lactic acid from water solution more effectively than does solvent extraction alone. Tertiary amine–chloroform systems extracted more than enough acid to neutralize the amine.

The solvent phases obtained by extraction with triamylamine and lower tertiary amines could be partially separated into solvent, free amine, and residual lactic acid by simple steam distillation; higher tertiary amines and didecyl- and dibenzylamine, the only secondary amines tested, did not steam-distill.

In one case where the solvent was 1-hexanol, the amine salt was esterified directly (*3*).

The initial lactic acid concentrations studied ranged from 1.5 to 32%.

Although the experiments demonstrated that lactic acid can be extracted effectively from water, more work on the recovery of lactic acid from the solvent phase is required for the development of a continuous process, which would be most desirable commercially. Such development is beyond the scope of this investigation.

ANALYTICAL METHODS

SOLVENT PHASE. After extraction, the total lactic acid content of the solvent phase was determined by shaking with an excess of aqueous standard alkali, separating the phases, and back-titrating in the presence of a mixed indicator (methyl red–methylene blue). When tested on a sample of pure dibutylammonium lactate, and known mixtures of lactic acid and tributylammonium lactate, this method gave results ranging from 0.1 to 1.5% high. This was sufficiently accurate.

AQUEOUS PHASE. Free Lactic Acid. In the experiments with primary and secondary amines, the free lactic acid in the water phase was found by titration to the phenolphthalein end point; the method was checked by titration of a known mixture. The total acid in the solvent phase and the free acid in the water phase were known, and the salt content of the water phase was found by difference.

In the experiments with tertiary amines, however, titration to the phenolphthalein end point was unsatisfactory because no break occurred in the pH curve at that point. Titration of the free acid in the presence of salts of tertiary amines, however, was possible, as shown in the case of tributylammonium lactate. The titration curve showed a break at pH 6 to 8, coinciding with the stoichiometric end point. At this point free amine was also liberated, and imparted a cloudiness to the solution. This "cloud point" was reproducible and accurate enough for the purpose; titrations of a mixture containing 1.312 milliequivalents (me.) per gram of tributylammonium lactate and 1.213 me. per gram of free lactic acid gave the following analyses for free acid: 1.221, 1.226, 1.215, 1.213, 1.252, and 1.222 me. per gram.

Total Acid. In most of the experiments with tertiary amines, the total lactic acid in the water phase was found by an ion exchange method, which exchanged trialkylammonium ions with hydrogen ions.

The cation exchange resin was Amberlite IR-100-H-AG; 16 grams were used in a 15-mm. column as a bed 175 mm. deep. The solution containing the free lactic acid and tertiary amine salt (totaling about 1.5 me. and diluted to 60 ml.) was passed dropwise through the column, which was then rinsed with successive 60-ml. portions of distilled water until the effluent titrated 0.005 me. or less per 60 ml. This was the average value of many 60-ml. blanks of distilled water.

The effluent of successive samples was titrated as lactic acid (phenolphthalein end point) and after correction for the blank the values were added to give the total acid.

After each analysis the column was regenerated with 100 ml. of 2 *N* hydrochloric acid, then backwashed with 4 liters of distilled water. The rate of backwashing was adjusted to expand the column bed 100%. The column was next rinsed forward until a 60-ml. sample gave a blank of 0.005 me. or less of acid.

A test mixture containing 1.247 me. per gram of lactic acid and 1.312 me. per gram of tributylammonium lactate (total lactic acid content 2.559 me. per gram) analyzed 2.575 me. per gram, a value 0.6% high. A second experiment analyzed 0.4% high. These results were satisfactory.

MATERIALS

Most of the amines were commercial samples, used without further purification. The solvents, likewise commercial materials, were checked for acidity before use and purified if necessary.

Solutions of pure lactic acid were prepared by diluting 80% edible grade acid, then heating the dilute solutions at 80° to 100° C. for about 2 days.

The crude acid studied was "22% lactic acid, dark grade" obtained commercially; it actually contained (potentiometric titration) 22.9% titratable acidity, computed as lactic

EVALUATION OF AMINES

Screening tests with various amines were made at room temperature (25° C.) on 8.7% acid (0.97 me. per ml.). It was first established that an organic solvent was necessary for good extraction. When 45 ml. of the dilute acid (43.5 me.) were mixed with 11 ml. (33.5 me.) of triamylamine, 82% of the amine layer dissolved, indicating relatively high water solubility of the amine salt. It would doubtless be possible to obtain better extraction by using a greater volume of amine, but there was no advantage in using excess amine as solvent for the amine salt.

TABLE I. EXTRACTION OF 8.7% LACTIC ACID AT 25° C. BY CHLOROFORM SOLUTIONS OF AMINES

Amines	Acid in Solvent Phase, %	Acid Remaining in Water Phase as Free Acid, %[a]	C_w[b]	K[b]
Primary				
n-Octyl	5[c]	3	0.78[c]	0.08[c]
n-Decyl	...	66[d]	...	...
n-Tetradecyl	...	[e]	...	...
n-Hexadecyl	...	[e]	...	...
Secondary				
Di-*n*-butyl	6	3	0.85	0.07
Di-*n*-decyl	89	0.5	0.11	7.5
Dicyclohexyl	54	3	0.45	1.2
Dibenzyl	37	64.5	0.61	0.7
Diphenyl	...	98	...	...
Tertiary				
Diethylbutyl	40	1.5	0.53	1.8
Tributyl	44.5	50.5	0.52	1.4
Triamyl	74	22	0.27	2.7
Trioctyl	83.5	11	0.18	4.5
Octadecyldimethyl	...	[e]	...	...
Tribenzyl	...	97	...	...
Dimethylaniline	...	97	...	...

[a] Fraction of initial acid in water phase as amine salt is found by subtracting from one the sum of fraction in solvent phase and fraction in water phase as free acid.

[b] $K = C_s/C_w$; C_s = total concentration of acid in solvent phase at equilibrium, me. per ml., C_w = total concentration of acid in water phase at equilibrium, me. per ml.

[c] Based on formol titration for total acid in water phase.

[d] Aqueous volume increased 11 ml., suggesting considerable solubilizing of organic phase in water.

[e] Mixture gelled, and phases did not separate on standing.

Accordingly, subsequent screening experiments were performed with chloroform as the organic solvent; chloroform was selected because of its successful use by Smith and Page (*15*) in similar experiments.

To 25 ml. of the acid solution in a buret were added 25 ml. of a chloroform solution containing an equivalent amount of the amine. The mixture was brought to equilibrium by mechanical rocking for 30 minutes; after separation of the phases the volume change of each phase was noted, and the phases were analyzed. For the more promising amines, over-all "distribution coefficients" were computed, defined by

$$K = \frac{C_s}{C_w}$$

where K is the distribution coefficient, C_s is the total concentration of lactic acid in the solvent phase, expressed as milliequivalents per milliliter, and C_w is the total concentration of lactic acid in the water phase, also in milliequivalents per milliliter.

The data, summarized in Table I, show that primary amines were not suitable; those of lower molecular weight gave water-soluble salts, and those of higher molecular weight gave salts of pronounced surface activity, as shown by solubilizing of solvent and by formation of gels.

Secondary amines were generally more satisfactory, although the lowest one tested gave a water-soluble salt. Di-*n*-decyl- was efficient, but a relatively large amount (10.5%) of the lactic acid remained in the water phase as salt. Dibenzylamine was less efficient, but within experimental error the water phase was free of salt. It is evident that an increase in the aromatic character of the amine led to a decrease in efficiency.

Best results were obtained with tertiary amines. It is evident

that efficiency increased with molecular weight of amine (tributyl- through trioctylamine); that a long side chain introduced undesirable surface activity (octadecyldimethylamine); and hat decreased efficiency accompanied increased aromatic character of the amine.

Some of these tertiary amines were accordingly studied in more detail. An experiment with a 24% excess of triamylamine left 20% of the initial acid in the water phase as free acid and an additional 2% as salt [the salt was determined by analysis for total acid by the method of Friedemann and Graeser (*8*)]. Hence it was concluded that an excess of this amine does not materially improve the extraction (Table I). An experiment with an 8% excess of trioctylamine showed a similar negligible improvement in efficiency.

When 25 ml. of a 32% solution of acid (91 me.) were extracted with 25 ml. of a chloroform solution containing 14.6 grams (53 me.) of trihexylamine, the solvent phase at equilibrium contained 77 me. of total lactic acid, and the water phase 14 me. Thus the solvent phase extracted 45% more acid than would be equivalent to the amine, an unexpected result. The value of K was 3.3, which compares favorably with the value obtained in experiments on tertiary amines employed in equivalent amounts (Table I).

EXTRACTION OF DILUTE LACTIC ACID

Because triamylamine was a fairly effective extracting agent (Table I) and also partially separable from its lactic acid salt by steam distillation, it was used in screening experiments on more dilute solutions. K was computed as before (Table I). The results are summarized in Table II. Although the experimental error became larger as the lactic acid concentration decreased, there appeared to be an increase in the K value for this system at the lower acid concentrations.

TABLE II. EXTRACTION OF DILUTE LACTIC ACID BY TRIAMYLAMINE IN CHLOROFORM AT 25° C.

Initial Concn. of Lactic Acid, %	C_w[a]	$K = \frac{C_s}{C_w}$[b]
8.7	0.27	2.7
4.3	0.18	4.4
4.3	0.17	4.6
1.5	0.026	5.1

[a] C_w = total concentration of lactic acid in water phase at equilibrium, me. per ml.
[b] C_s = total concentration of lactic acid in solvent phase at equilibrium, me. per ml.

EVALUATION OF SOLVENTS

Earlier work in esterifying amine salts of lactic acid with alcohols (*3*) suggested the possibility of using an amine-alcohol mixture as the extracting phase, and then subjecting the solvent phase to conditions which would result in synthesis of the ester:

$$CH_3CHOHCO_2NHR_3 + R'OH = CH_3CHOHCOOR' + R_3N + H_2O$$

Hence some evaluation tests were made on alcohols as solvents; for comparison, a few other organic solvents were also evaluated.

In each evaluation experiment, 25 me. as an 8.7% solution of lactic acid were treated with a slight excess of the amine dissolved in 20 ml. of solvent. After mechanical mixing for 30 minutes, the volume of each phase was read, and the solvent phase was analyzed for lactic acid. As before, distribution coefficients were computed for each solvent (Table III).

From these results, it is evident that

TABLE III. EVALUATION OF SOLVENTS[a] IN EXTRACTION OF LACTIC ACID BY TRIAMYLAMINE AT 25° C.

Solvent	C_s[b]	$K = \frac{C_s}{C_w}$[c]
Isobutyl alcohol	0.66	2.6
n-Butyl alcohol	0.60	2.2
n-Amyl alcohol	0.63	2.3
sec-Amyl alcohol	0.64	2.3
tert-Amyl alcohol	0.57	1.6
Isoamyl alcohol	0.68	3.1
3-Pentanol	0.64	2.3
Methyl isobutyl carbinol	0.58	1.6
3-Heptanol	0.55	1.4
2-Ethylhexanol	0.61	1.7
2-Octanol	0.80	5.3
Chloroform	0.73	2.7
Pinene	0.20	0.3
Ethyl acetate	0.52[d]	0.7[d]

[a] Ether, petroleum ether, carbon tetrachloride, and benzene had distribution coefficients of 0.3 or less. Nitromethane dissolved and benzyl alcohol separated at an excessively low rate.
[b] C_s = total concn. of lactic acid in solvent phase at equilibrium, me. per ml.
[c] C_w = total concn. of lactic acid in water phase at equilibrium, me. per ml.
[d] Computed from free acidity in water phase.

alcohols as a class are effective extracting agents. The data of Table III indicate that most of the solvents listed are efficient enough to be used in a continuous extraction process with only a few theoretical plates. Hence, final selection would have to be made on the basis of other factors, such as cost, water solubility, and performance with crude acid. The use of alcohols, however, is especially desirable because the esters made directly through the amine salts (*4*) could be used as intermediates for plasticizers of the type described by Rehberg and Dixon (*13*).

SEMICONTINUOUS EXTRACTIONS

The extraction work was next extended to a semicontinuous process that employs the apparatus of Bewick, Currah, and Beamish (*2*). These extractions were made at room temperature and with the solvent-amine mixture as the continuous phase.

It was hoped that this equipment would make possible the calculation of a "distribution factor" (*2*), and also would permit a detailed study of changes of this factor with concentration. Analysis of successive samples of effluent, however, did not provide concordant results, and these aims were not realized, possibly because of the high distribution coefficient.

The results are summarized in Table IV. In the presence of excess acid, tertiary amines in chloroform extracted more than an equivalent amount of acid (experiments 1 and 2).

It is evident also that despite the high efficiency of trioctylamine (Table I), combination of this amine with 1-hexanol was less effective than mixtures of other amines with chloroform. Neverthless, the extraction in experiment 5 was great enough to indicate that a few extraction stages would permit high recovery of the acid from water in a continuous process.

RECOVERY OF LACTIC ACID FROM THE SOLVENT PHASE

When the extraction experiments had demonstrated that lactic acid could be extracted much more efficiently by amine-solvent mixtures than by solvents alone (*11*), it became important

TABLE IV. SEMICONTINUOUS EXTRACTION OF LACTIC ACID BY AMINES IN ORGANIC SOLUTION

Expt. No.	Acid Strength, % by Wt.	Acid Used, Me.	Pumping Rate, Ml./Min.	Volume of Chloroform Phase, Ml.	Amine Used, Me.	Total Acid in Effluent, Me.	Total Acid in Solvent, Me.
1	32	626	2	200	Triamyl, 415	91	535
2	32	1060	3	300	Trihexyl, 403	268	792
3	9.1	202	0.7	100	Didecyl, 108	106	96
4	1.5	85	1.8	175	Triamyl, 85	21[a]	64
5	32	466	2.6	180[b]	Trioctyl, 330	219	247

[a] 8 me. as free acid; rest as amine salt.
[b] Solvent was *n*-hexanol (530 me.); see text.

to investigate the recovery of the lactic acid from the solvent phase, where the acid was present mainly as the amine salt. A simple steam distillation, which might strip away solvent and amine and leave the acid in water solution, would be especially desirable. Preliminary experiments showed that this process was at least partially operable with triamyl- and tributylamine.

Thus the solvent phase from experiment 1, Table IV, was steam-distilled. Solvent recovery was quantitative, but only 35 grams (36.5%) of the amine distilled. The aqueous residue from this distillation contained 300 me. of free lactic acid and 200 me. of the amine salt. The salt represented an additional 46.5 grams (48.5%) of the amine; hence, 85% was accounted for.

Steam distillation of the chloroform layers from experiments with didecyl-, trihexyl-, trioctyl-, and dibenzylamine resulted in excellent solvent recovery, but negligible amine distillate. From the residue of the experiment with didecylamine, crystalline didecylammonium lactate was obtained, melting point 79–80° C. after recrystallization from ether.

ANALYSIS. Calculated for $C_{23}H_{49}O_3N$: C, 71.3; H, 12.7; N, 3.61%. Found: C, 71.0; H, 12.8; N, 3.74%.

From the residue of the trioctylamine experiment, crystals (believed to be trioctylammonium lactate) were obtained, melting point 70–70.5° C. after recrystallization from ether. The residues from the other two experiments did not crystallize. These experiments showed that triamylamine was the highest tertiary amine that could be steam-distilled from the chloroform solution of its lactic acid salt under ordinary conditions.

To examine another recovery method, a semicontinuous extraction was performed, with trioctylamine-hexanol mixture as the solvent phase (experiment 5, Table IV). The solvent phase was subjected to esterification (*3*) and 24 grams of hexyl lactate were obtained, representing a conversion of 30% of the initial acid to ester. The yield based on the extracted acid was 57%.

EXTRACTION OF LACTIC ACID FROM CRUDE DARK AQUEOUS SOLUTIONS

When 20 ml. (51 me.) of the crude dark solution were batch-extracted with 50 ml. of a chloroform solution containing a 24% excess of triamylamine, only 3.5% of the initial free acid remained unextracted. A similar batch experiment with 3-heptanol as solvent yielded an aqueous phase containing 9% of the initial free acid. An aliquot of the heptanol phase was treated with decolorizing carbon and filtered. Analysis showed that the solvent layer treated in this way would contain 68% of the initial acid. Another aliquot of the heptanol layer was steam-distilled to remove solvent and some amine, and the dark residue thus obtained was treated with decolorizing carbon. Analysis of the light straw-colored filtrate indicated that this water solution contained 78% of the initial acid.

Another batch experiment, with *tert*-amyl alcohol as solvent, yielded an aqueous phase containing 6% of the initial acid. Analysis of an aliquot of the solvent phase showed 81% of the initial acid; the residue after steam distillation of another aliquot contained 74% of the initial acid as a light amber solution. The *K* value for this experiment was 12, suggesting that acid is more readily extracted from its crude solution than from water alone.

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